

# NATIONAL BUREAU OF STANDARDS REPORT

9650

Progress Report

on

ISOTHERMAL DIFFUSION IN THE DILUTE RANGE OF THE

SYSTEM  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ . I - THEORY



U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

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by

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Abstract

The equations describing isothermal diffusion in the dilute range of the ternary system, containing a weak electrolyte,  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ , are derived in two ways, first, assuming that the components are electroneutral species and, second, considering the actual ionic species present in solution. It is shown that the two models are thermodynamically equivalent. The theory permits the calculation of the four fundamental diffusion coefficients (phenomenological coefficients) in the concentration range where the Debye-Hückel theory suffices for the calculation of ionic activity coefficients. Therefore, the equations can be used to test the Onsager reciprocal relations for the diffusion process in the above system. The ionic model allowed derivation of expressions for calculating practical diffusion coefficients for the electroneutral components from the limiting equivalent conductances of the ions in solution; thus, it becomes possible to compare experimental diffusion coefficients with those anticipated theoretically.



relations, it is necessary to calculate the partial derivatives of activity coefficients with respect to the concentration of the components. Previous treatments of this problem in ternary systems have either assumed invariance of activity coefficients with concentration<sup>10</sup> or have used assumptions applicable to symmetric electrolytes<sup>11</sup>. The present treatment applies to the ternary system  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$  in the concentration range where the Debye-Hückel theory has been shown<sup>12,13</sup> to describe adequately ionic activity coefficients. Derivations will be given for two models in which electroneutral components and ionic constituents are considered, respectively. It will be shown that these two models are thermodynamically equivalent.

## 2.0. Procedure

### 2.1. Selection of model

All the equilibrium properties of the ternary system referred to in this paper can be defined in terms of the components  $\text{Ca}(\text{OH})_2$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{O}$ . For diffusion

purposes, the number of components,  $C'$ , may be obtained from the expression  $C' = n - r$ , in which  $n$  is the total number of chemical species, ionic and electroneutral, present in the system and  $r$  is the number of restrictions operating on those species. Usually, for the case of strong electrolytes the only restriction is electroneutrality. If  $\text{Ca}(\text{OH})_2$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{O}$  are selected as components, in general,  $n$  would comprise eight constituents:  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{H}^+$ ,  $\text{Ca}^{++}$ , and  $\text{OH}^-$ . The system would have five restrictions: the three expressions for the three ionization constants of  $\text{H}_3\text{PO}_4$ , the expression for the ionization constant of  $\text{H}_2\text{O}$ , and the condition of electroneutrality. Therefore, the system is ternary.

It is neither fruitful nor realistic to consider all the foregoing constituents and restrictions. The derivations would become unnecessarily complicated; besides, because of the magnitudes of the ionization constants of  $\text{H}_3\text{PO}_4$ , in any given system only two phosphate containing species are present in significant

concentrations. Furthermore, as done by other investigators<sup>10,14</sup>, it will be assumed that the solvent,  $H_2O$ , is undissociated. If now, neutral components that do not contain the ion  $OH^-$  are selected,  $n$  will be equal to five ( $H_2O$ , two phosphate-containing species,  $Ca^{++}$ , and  $H^+$ ), and  $r$  will be two (equilibrium between the two phosphate-containing species and electroneutrality); hence, the simplified model is ternary for diffusion purposes. The two phosphate species considered here are  $H_2PO_4^-$  and  $HPO_4^{=}$  which are the only species present in significant concentrations in the experimental pH range of 4 to 6.5. The other two components, besides  $H_2O$ , correspond to electroneutral combinations of the ions considered and their selection is arbitrary. For convenience,  $CaHPO_4$  and  $H_3PO_4$  are selected here, but the treatment would apply equally well to, for example,  $CaHPO_4$  and  $Ca(H_2PO_4)_2$ .



## 2.2 Derivations

The diffusion coefficients in the present investigation were obtained in a cell-fixed frame of reference (a porous diaphragm cell). However, for the range of the dilute solutions considered here, it is reasonable to assume that the partial molar volumes of the components are independent of concentration. Under these conditions, these practical diffusion coefficients,  $(D_{ij})_c$ , become identical with those referred to a constant-volume frame of reference,  $(D_{ij})_v$ .<sup>10,15</sup> Furthermore, the solvent-fixed diffusion coefficients,  $(D_{ij})_0$ , are related to the volume-fixed frame of reference<sup>10,14</sup> by

$$(D_{ij})_0 = (D_{ij})_v + \frac{C_i}{C_0 \bar{v}_0} \sum_{k=1}^q \bar{v}_k (D_{kj})_v \quad \begin{matrix} i = 1, \dots, q \\ k = 1, \dots, q \end{matrix}$$

in which  $C_i$  and  $C_0$  are the concentrations of the  $i$ th components and the solvent, respectively;  $\bar{v}_0$  and  $\bar{v}_k$ , the partial molar volumes of the solvent and the component  $K$ , respectively; the summation is taken over  $q$  components, excluding the solvent. It is apparent that at

infinite dilution,  $(D_{1,j})_0 = (D_{1,j})_v$ ; even for concentrations about 1M, the two sets of coefficients do not differ by more than 1 to 5 per cent<sup>16</sup>.

For the foregoing reasons, it is assumed that the derivations shown here, although strictly applicable only to a solvent-fixed frame of reference, are valid for the systems under consideration, since their highest concentration is in the order of  $10^{-3}M$ .

### Electroneutral Model

According to the principles of non-equilibrium thermodynamics<sup>17,18</sup>, the flow for the component  $i$ ,  $J_i$ , in a ternary system may be described by

$$J_i = - \sum_{j=0}^2 \tilde{L}_{ij} (\partial \mu_j / \partial x) \quad i = 0, 1, 2 \quad (1)$$

in which  $\tilde{L}_{ij}$  are phenomenological coefficients and the quantity within parenthesis is the gradient of the chemical potential  $\mu_j$  for component  $j$  along  $x$ ; the summation in (1) includes the solvent designated by the subscript zero.

From the Gibbs-Duhem equation, at constant temperature and pressure, it is obtained

$$\sum_{j=0}^2 C_j \partial \mu_j / \partial x = 0 \quad (2)$$

solution of equation (2) for  $\partial \mu_0 / \partial x$  and substitution into equations (1) gives

$$J_i = - \sum_{j=1}^2 L_{ij} (\partial \mu_j / \partial x) \quad i = 1, 2 \quad (3)$$

In equations (3), the flow of the component  $i$  is given in terms of the chemical potential gradients of the solutes; therefore, the phenomenological coefficients, usually called "fundamental diffusion coefficients"  $L_{ij}$ , display Onsager's reciprocal relations<sup>14</sup>.

The flow  $J_i$  in equations (3) may now be given in terms of practical diffusion coefficients,  $D_{ij}$ . In a ternary system, only the concentrations,  $C_1$  and  $C_2$ , of two of the components are independent variables. Therefore,

$$\frac{\partial \mu_j}{\partial x} = \sum_{k=1}^2 \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial x} \quad j = 0, 1, 2 \quad (4)$$

Substitution of equation (4) into equation (3) gives

$$J_i = - \sum_{j=1}^2 L_{ij} \sum_{k=1}^2 \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial X} \quad (5)$$

or

$$J_i = - \sum_{k=1}^2 D_{ik} \frac{\partial C_k}{\partial X} \quad i = 1, 2 \quad (6)$$

in which the practical diffusion coefficients,  $D_{ik}$  are given by

$$D_{ik} = \sum_{j=1}^2 L_{ij} \frac{\partial \mu_j}{\partial C_k} \quad \begin{matrix} i=1, 2 \\ k=1, 2 \end{matrix} \quad (7)$$

The four practical diffusion coefficients  $D_{ik}$  can be obtained through a minimum of two diffusion experiments, by the use of equations (6) with the appropriate boundary conditions. From equations (7), the following relations may be obtained by solving for the  $L_{ij}$ :

$$\begin{aligned} L_{11} &= (D_{11} \mu_{22} - D_{12} \mu_{21})/s \\ L_{12} &= (D_{12} \mu_{11} - D_{11} \mu_{12})/s \\ L_{21} &= (D_{21} \mu_{22} - D_{22} \mu_{21})/s \\ L_{22} &= (D_{22} \mu_{11} - D_{21} \mu_{12})/s \end{aligned} \quad (8)$$

in which  $\mu_{ij}$  stand for the partial derivatives  $\partial \mu_i / \partial C_j$  and the denominator  $s$  is given by

$$S = \mu_{11}\mu_{22} - \mu_{12}\mu_{21}$$

Equations (8), previously used by other investigators<sup>14,15</sup> permit to calculate the fundamental diffusion coefficients,  $L_{ij}$ , from practical diffusion coefficients that are determined experimentally, provided that the values of the various partial derivatives are known. The method for evaluation of these derivatives is given next.

The chemical potential of the  $i$ th component,  $\mu_i$ , is defined in terms of its activity  $a_i$ , by

$$\mu_i = \mu_i^0 + RT \ln a_i$$

in which  $\mu_i^0$  is a constant under constant temperature,  $T$ , and pressure, and  $R$  is the gas constant. The partial derivatives,  $\mu_{ij}$ , are given by

$$\mu_{ij} = \frac{RT}{a_i} a_{ij} \quad \begin{matrix} i = 1, 2 \\ j = 1, 2 \end{matrix} \quad (9)$$

in which  $a_{ij}$  represents the partial derivatives  $\partial a_i / \partial C_j$ .

Thus, the evaluation of  $\mu_{ij}$  is accomplished if appropriate expressions of  $a_{ij}$  are available.



As shown in equations (46) and (47) in Appendix 1, the activities,  $a_1$  and  $a_2$ , for components 1 and 2 ( $\text{CaHPO}_4$  and  $\text{H}_3\text{PO}_4$ , respectively) are functions of their concentrations  $C_1$  and  $C_2$ . Other parameters in those expressions (hydrogen activity and ionic activity coefficients) are also functions of  $C_1$  and  $C_2$ . Therefore

$$a_{1j} = \left( \frac{\partial a_1}{\partial C_j} \right)_{C_k} = \left( \frac{\partial a_1}{\partial C_j} \right)_{C_k, H, \gamma_l} + \left( \frac{\partial a_1}{\partial H} \right)_{C_j, C_k, \gamma_l} \left( \frac{\partial H}{\partial C_1} \right)_{C_k} + \sum_l \left( \frac{\partial a_1}{\partial \gamma_l} \right)_{C_j, C_k, H} \left( \frac{\partial \gamma_l}{\partial C_j} \right)_{C_k} \quad \left\{ \begin{array}{l} j = 1, 2 \\ j = 1, 2 \\ k = 1, 2 \\ j \neq k \end{array} \right. \quad (10)$$

in which  $H$  represents the ionic activity of hydrogen, and  $\gamma_l$  represents the activity coefficient of each of the  $l$  ions assumed to be present in the system,  $\text{Ca}^{++}$ ,  $\text{H}^+$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{--}$ .

The electroneutrality function  $E$ , equation (42) in Appendix 1, which will be used later, is defined on the basis that only these ions are present. (The presence of ion pairs is ignored.) In the subsequent equations through equation (19), indexes  $i$ ,  $j$ , and  $k$ , assume the same values as in equation (10).

In the dilute range of the ternary system under consideration, it has been shown<sup>12,13</sup> that the Debye-Hückel theory provides an adequate expression for the calculation of ionic activity coefficients. Thus,  $\gamma_\ell$  are explicit functions of the ionic strength  $I$ . Therefore, the second factor in the summation term of equation (10) becomes

$$\left( \frac{\partial \gamma_\ell}{\partial C_j} \right)_{c_k} = \frac{d\gamma_\ell}{dI} \left( \frac{\partial I}{\partial C_j} \right)_{c_k} \quad (11)$$

By substitution of equation (11) into equation (10) and making

$$\sum_\ell \left( \frac{\partial a_i}{\partial \gamma_\ell} \right)_{c_j, c_k, H} \frac{d\gamma_\ell}{dI} = a_i^*$$

equation (10) becomes

$$a_{ij} = \left( \frac{\partial a_i}{\partial C_j} \right)_{c_k, H, \gamma_\ell} + \left( \frac{\partial a_i}{\partial H} \right)_{c_j, c_k, \gamma_\ell} \left( \frac{\partial H}{\partial C_j} \right)_{c_k} + \quad (12)$$

$$a_i^* \left( \frac{\partial I}{\partial C_j} \right)_{c_k}$$

By differentiation of equation (43) in Appendix 1, it follows that

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_\ell} + \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{c_k} \quad (13)$$

$$\sum_{\ell} \left(\frac{\partial I}{\partial \gamma_\ell}\right)_{c_j, c_k, H} \left(\frac{\partial \gamma_\ell}{\partial C_j}\right)_{c_k}$$

By substitution of equation (11) into (13) and making

$$\sum_{\ell} \left(\frac{\partial I}{\partial \gamma_\ell}\right)_{c_j, c_k, H} \frac{d\gamma_\ell}{dI} = I^*$$

equation (13) becomes

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_\ell} + \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{c_k} + I^* \left(\frac{\partial I}{\partial C_j}\right)_{c_k} \quad (14)$$

Solving equation (14) for  $(\partial I / \partial C_j)_{c_k}$

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left[ \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_\ell} + \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{c_k} \right] (1 - I^*)^{-1} \quad (15)$$

Substitution of equation (15) into equation (12) gives an expression for  $a_{ij}$  in terms of partial derivatives that can be readily calculated from experimental measurements, except for the derivative  $(\partial H / \partial C_j)_{c_k}$ . The derivation for  $(\partial H / \partial C_j)_{c_k}$  is given next.

Differentiation of the electroneutrality function  $E$ , equation (42) in Appendix 1, gives

$$\left( \frac{\partial E}{\partial C_j} \right)_{c_k} = 0 = \left( \frac{\partial E}{\partial C_j} \right)_{c_k, H, \gamma_l} + \left( \frac{\partial E}{\partial H} \right)_{c_j, c_k, \gamma_l} \left( \frac{\partial H}{\partial C_j} \right)_{c_k} + \sum_l \left( \frac{\partial E}{\partial \gamma_l} \right)_{c_j, c_k, H} \left( \frac{\partial \gamma_l}{\partial C_j} \right)_{c_k} \quad (16)$$

By substitution of equation (11) into equation (16) and making

$$\sum_l \left( \frac{\partial E}{\partial \gamma_l} \right)_{c_j, c_k, H} \frac{d\gamma_l}{dI} = E^*$$

equation (16) becomes

$$\left(\frac{\partial E}{\partial C_j}\right) = 0 = \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_\ell} + \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{c_k} + E^* \left(\frac{\partial I}{\partial C_j}\right)_{c_k} \quad (17)$$

Substitution of equation (15) into equation (17) gives the solution for  $(\partial H / \partial C_j)_{c_k}$ ,

$$\left(\frac{\partial H}{\partial C_j}\right)_{c_k} = - \frac{(1-I^*) \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_\ell}}{(1-I^*) \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell}} \quad (18)$$

Substitution of equation (18) into equation (15) gives

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \frac{\left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_\ell} \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_\ell} - \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell} \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_\ell}}{(1-I^*) \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_\ell}} \quad (19)$$

The right-hand terms in equations (18) and (19) involve quantities that can be readily calculated from experimental measurements. The actual expressions used for such calculations are given in Appendix 2. Substitution of equations (11), (18) and (19) into equation (10) gives the needed expression for the evaluation of  $a_{1j}$ ; then, by the use of equation (9), evaluation of  $u_{1j}$  is

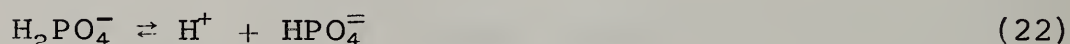


accomplished, and substitution of the  $\mu_{ij}$  into equations (8) permits the calculation of the fundamental diffusion coefficients,  $L_{ij}$ , and, therefore, the testing of the Onsager's reciprocal relations.

### Ionic Model

In the foregoing treatment, the components have been considered as neutral species, although in defining their activities, their ionic nature was taken into account. Consideration of an ionic model for the present system is advantageous in that practical diffusion coefficients can be calculated for the electroneutral components on the basis of ionic conductances<sup>10</sup>. It is then possible to compare the practical diffusion coefficients derived here with those obtained experimentally.

The ionic model selected here is given in equations (20) to (22)



This ionic model implies that there is no undissociated  $\text{H}_3\text{PO}_4$ , an assumption which is valid for the pH range considered here. It will be shown now that this system is thermodynamically equivalent to the one in which  $\text{CaHPO}_4$  and  $\text{H}_3\text{PO}_4$  are considered as the neutral components. In the following derivations,  $i$  represents the constituents  $\text{CaHPO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{PO}_4^-$  and  $j$  represents the ionic species in equations (20) to (22). The numerals 1, 2 and 3 are used for these three constituents, respectively and the numerals 4, 5 and 6 represent the ions  $\text{Ca}^{++}$ ,  $\text{HPO}_4^{--}$  and  $\text{H}^+$ , respectively.

The stoichiometric coefficients in the right-hand terms of equations (20) to (22) are represented by  $\nu_{ij}$ . For example,  $\nu_{14}$  is the stoichiometric coefficient for the  $\text{Ca}^{++}$  that comes from  $\text{CaHPO}_4$  and  $\nu_{15}$  is for the  $\text{HPO}_4^{--}$  that comes from the  $\text{CaHPO}_4$ . The numerical values for the  $\nu_{ij}$ 's are:  $\nu_{14} = \nu_{15} = \nu_{25} = \nu_{35} = \nu_{36} = 1$ ;  $\nu_{16} = \nu_{24} = \nu_{34} = 0$ ;  $\nu_{26} = 2$ .

On the basis of the ionic model, the entropy production,  $\sigma T$ , in the diffusion system is given by<sup>12, 26</sup>

$$\sigma T = \sum_{j=3}^6 J_j \bar{X}_j = \sum_{j=4}^6 J_j \bar{X}_j + J_3 \bar{X}_3 \quad (23)$$

in which  $J_j$  represents the diffusion flow of the  $j$ th ion and  $\bar{X}_j$  its generalized driving force, in this case, its electrochemical potential gradient;  $\sigma$  is the rate of entropy production at temperature  $T$ .

We consider now as new generalized forces the chemical potential gradients,  $X_i$ , of the neutral components 1 and 2 and the electrochemical potential  $\bar{X}_3$ . The transformation equations for the new forces are

$$X_i = \sum_{j=4}^6 v_{ij} \bar{X}_j \quad (i=1, 2) \quad (24)$$

$$\bar{X}_3 = \sum_{j=4}^6 v_{3j} \bar{X}_j$$

which are linear combinations of the old forces  $\bar{X}_j$ .

The transformation equations for the new flows, derived from the mass balance condition in equations (20) to (22), are

$$J_j = \sum_{i=1}^2 v_{ij} J_i - v_{3j} J_3 \quad (j=4 \text{ to } 6) \quad (25)$$

Substitution of equation (25) into (23) gives

$$\sigma T = \sum_{i=1}^2 \sum_{j=4}^6 v_{ij} \bar{X}_j J_i - J_3 \left( \sum_{j=4}^6 v_{3j} \bar{X}_j - \bar{X}_3 \right) \quad (26)$$

But, according to equations (24) the summation term within parenthesis equals  $\bar{X}_3$ , therefore, the quantity within parenthesis vanishes and

$$\sigma T = \sum_{i=1}^2 J_i X_i \quad (27)$$

hence, the ionic model is thermodynamically equivalent to the diffusion system in which the neutral compounds  $\text{CaHPO}_4$  and  $\text{H}_3\text{PO}_4$  are considered as components.

The procedure to calculate fundamental diffusion coefficients for neutral components from ionic conductances has been given in detail by Wendt<sup>10</sup> and it was tested by the same author with diffusion data<sup>21</sup> for the system  $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ . For this reason, only a summary of our derivation is given next in which we apply Wendt's treatment to the present system. We use the same terminology except that his  $L_{ij}$  (for ions) corresponds to our  $\Gamma_{ij}$ , and his  $a_{ij}$  correspond to our  $\alpha_{ij}$ .

The diffusion flows  $J_j$  of the  $j$  ions are related to the chemical potential gradients,  $X_n$ , of the two neutral components by

$$J_j = v^{-1} \sum_{n=1}^2 \sum_{k=3}^6 \alpha_{kn} X_n \Omega_{jk} \quad (j=3 \text{ to } 6) \quad (28)$$

in which  $v$  is the value of the determinant of the  $v_{ij}$  matrix (equal to -1 in the present case);  $\alpha_{kn}$ , the elements of the matrix  $[\alpha_{kn}]$ , have the numerical values  $\alpha_{31} = \alpha_{32} = \alpha_{51} = \alpha_{61} = 0$ ,  $\alpha_{33} = \alpha_{41} = \alpha_{62} = 1$ ,  $\alpha_{52} = \alpha_{63} = 1$ ,  $\alpha_{43} = 2$ ,  $\alpha_{53} = -2$ ; the coefficients  $\Omega_{jk}$  are given by



$$\Omega_{jk} = \delta_{jk} \Gamma_{jk} - \frac{\Gamma_{jj} \alpha_{j3} \Gamma_{kk} \alpha_{k3}}{\sum_{q=3}^6 \Gamma_{qq} \alpha_{q3}^2} \quad \begin{matrix} j=3 \text{ to } 6 \\ k=3 \text{ to } 6 \end{matrix} \quad (29)$$

In equation (29),  $\delta_{jk}$  is the Kronecker delta (it has the value 1 for  $j=k$ , and zero for  $j \neq k$ ), and the  $\Gamma$ 's are the main terms of the fundamental diffusion coefficients for the subscripted ions, 3 to 6. Equation (29) is consistent with Wendt's assumption<sup>10</sup> that the coefficients  $\Gamma_{jk}$  are zero for  $j \neq k$ . These ionic coefficients can be calculated from

$$\Gamma_{jj} = \lambda_j^{\circ} C_j |Z_j| F^2 \times 10^7 \quad j=3 \text{ to } 6 \quad (30)$$

in which  $\lambda_j^{\circ}$  is the limiting equivalent conductance of the ion  $j$ ,  $C_j$  its molarity,  $|Z_j|$  the absolute value of its valance and  $F$  is the Faraday constant (96,493 coulombs per equivalent of charge). Values used for  $\lambda_j^{\circ}$  in this investigation are given in Appendix 1.

Expanding equation (25) and solving for  $J_1$  and  $J_2$  (using the numerical values for the corresponding  $v_{ij}$ ) we get

$$J_1 = J_4 \quad (31)$$

$$J_2 = \frac{1}{2} (J_3 + J_6) \quad (32)$$

The expressions for the ionic flows  $J_3$ ,  $J_4$  and  $J_6$  given by equation (28) can now be substituted into equations (31) and (32) to obtain

$$J_1 = - \sum_{n=1}^2 \sum_{k=3}^6 \alpha_{kn} X_n \Omega_{4k} \quad (32)$$

$$J_2 = - \frac{1}{2} \sum_{n=1}^2 \sum_{k=3}^6 \alpha_{kn} X_n \Omega_{6k} - \frac{1}{2} \sum_{n=1}^2 \sum_{k=3}^6 \alpha_{kn} X_n \Omega_{3k} \quad (33)$$

But from equation (3) we can also write

$$J_1 = - \sum_{n=1}^2 L_{1n} X_n \quad (34)$$

$$J_2 = - \sum_{n=1}^2 L_{2n} X_n \quad (35)$$

Through a comparison of the coefficients of  $X_n$  in equations (34) and (35) with those in equations (32) and (33) respectively, it is obtained

$$L_{1n} = \sum_{k=3}^6 \alpha_{kn} \Omega_{4k} \quad n=1, 2 \quad (36)$$

$$L_{2n} = \frac{1}{2} \sum_{k=3}^6 \alpha_{kn} (\Omega_{6k} + \Omega_{3k})$$

Equations (36) together with (29) and (30), permit the calculation of theoretical fundamental diffusion coefficients,  $L_{1j}$ , from a knowledge of the limiting conductance of the ions involved, subject to the assumption adopted (ideal ionic behavior). These coefficients are compared with those calculated from experimental data in the results section; likewise, a comparison is made between the values for the practical diffusion coefficients,  $D_{1j}$ , obtained experimentally and those calculated by substituting the  $L_{1j}$  obtained in equation (36) into equation (8), using the expressions for  $\mu_{1j}$  previously derived.

## APPENDIX 1

Symbols:

- $C_1$  = molar concentration of  $\text{CaHPO}_4$
- $C_2$  = molar concentration of  $\text{H}_3\text{PO}_4$  used in preparation of solution
- $P_0$  = molar concentration of undissociated  $\text{H}_3\text{PO}_4$
- $P_1$  = molar concentration of  $\text{H}_2\text{PO}_4^-$
- $P_2$  = molar concentration of  $\text{HPO}_4^{--}$
- $\gamma_1$  = molar activity coefficient for  $\text{H}_2\text{PO}_4^-$
- $\gamma_2$  = molar activity coefficient for  $\text{HPO}_4^{--}$
- $\gamma_3$  = molar activity coefficient for  $\text{Ca}^{++}$
- $\gamma_4$  = molar activity coefficient for  $\text{H}^+$
- $[\text{H}]$  = molar concentration of  $\text{H}^+$
- $\text{H}$  = activity of  $\text{H}^+$
- $K_1$  = first ionization constant of  $\text{H}_3\text{PO}_4$ ,  $7.10_8 \times 10^{-3}$  (22)
- $K_2$  = second ionization constant of  $\text{H}_3\text{PO}_4$ ,  $6.33_8 \times 10^{-8}$  (23)
- $(P_2)$  = activity of  $\text{HPO}_4^{--}$
- $\lambda^{\circ}_3$  = limiting equivalent conductance of  $\text{H}_2\text{PO}_4^-$ , 32.3 (24)
- $\lambda^{\circ}_4$  = limiting equivalent conductance of  $\text{Ca}^{++}$ , 59.50 (25)
- $\lambda^{\circ}_5$  = limiting equivalent conductance of  $\text{HPO}_4^{--}$ , 43.7 (26)
- $\lambda^{\circ}_6$  = limiting equivalent conductance of  $\text{H}^+$ , 349.8<sub>1</sub> (25)

# APPENDIX 1 (continued 2)

The total molar concentration of phosphorus in the solutions of  $\text{CaHPO}_4$  in dilute  $\text{H}_3\text{PO}_4$  is given by  $(C_1 + C_2)$ . The balance equation for phosphorus, for solutions with pH values below 7 ( $\text{PO}_4^{--}$  is negligible), may be written

$$(C_1 + C_2) = P_0 + P_1 + P_2 \quad (37)$$

in which  $P_0$  is the molar concentration of undissociated  $\text{H}_3\text{PO}_4$ . The quantities  $P_0$  and  $P_1$  may be written in terms of  $P_2$  by the use of the expressions for the first and second ionizations of  $\text{H}_3\text{PO}_4$ ; then, solving equation (37) for  $P_2$  gives

$$P_2 = (C_1 + C_2) / \gamma_2 \left( \frac{1}{\gamma_2} + \frac{H}{K_2 \gamma_1} + \frac{H^2}{K_1 K_2} \right) \quad (38)$$

In the pH range 4 to 5, the first and third terms within the parenthesis in the denominator of equation (38) are negligible compared to the second one. Between pH 5 and 7 only the first and second terms in the parenthesis need to be considered. The maximum error introduced in the value of  $P_2$  by these simplifications amounts to 1 per cent.



# APPENDIX 1 (continued 2)

Calling  $f_2$  the quantity within parenthesis in the denominator of equation (38)

$$P_2 = (C_1 + C_2)/\gamma_2 f_2 \quad (39)$$

and by substitution of equation (39) into the expression for the second ionization of  $H_3PO_4$ , it is obtained

$$P_1 = (C_1 + C_2)H/f_2 \gamma_1 K_2 \quad (40)$$

The function E, that defines electroneutrality, is

$$E = 0 = 2C_1 + \frac{H}{\gamma_4} - 2 P_2 - P_1 \quad (41)$$

substitution of equations (39) and (40) into (41) gives

$$E = 0 = 2C_1 + \frac{H}{\gamma_4} - \frac{(C_1 + C_2)}{f_2} \left[ \frac{H}{\gamma_1 K_2} + \frac{2}{\gamma_2} \right] \quad (42)$$

The ionic strength, I, is given by

$$I = 2C_1 + \frac{H}{2\gamma_4} + \frac{C_1 + C_2}{2f_2} \left[ \frac{H}{\gamma_1 K_2} + \frac{4}{\gamma_2} \right] \quad (43)$$

For brevity in the expressions given in Appendix 2, we shall define the quantities within square brackets in equations (42) and (43) as

APPENDIX 1 (continued 3)

$$Q = \frac{H}{K_2 \gamma_1} + \frac{2}{\gamma_2} \quad (44)$$

$$G = \frac{H}{K_2 \gamma_1} + \frac{4}{\gamma_2} \quad (45)$$

The activities of  $\text{CaHPO}_4$  and  $\text{H}_3\text{PO}_4$  in solution are given by equations (46) and (47), respectively.

$$a_1 = \frac{(C_1^2 + C_2 C_1) \gamma_3}{f_2} \quad (46)$$

$$a_2 = \frac{(C_1 + C_2) H}{f_1 K_1} \quad (47)$$

The function  $f_1$  in equation (47) is defined by

$$f_1 = \frac{H}{K_1} + \frac{K_2}{H \gamma_2} + \frac{1}{\gamma_1} \quad (48)$$

The ionic activity coefficients,  $\gamma_\ell$ , are calculated from the Debye-Hückel theory

$$\ln \gamma_\ell = - \frac{AZ_\ell^2 \sqrt{I}}{1 + B\alpha_\ell \sqrt{I}} \quad (49)$$

in which the constants A and B, dependent on temperature and the dielectric constant of water, have numerical values of 0.5092 and  $0.3286 \times 10^8$ , respectively (27) at 25°C;  $Z_\ell$  is the valence of the  $\ell$ th ion, and  $\alpha_\ell$  its

APPENDIX 1 (continued 4)

distance of closest approach. Numerical values for  $\alpha_{\ell}$  (28) are:  $\text{Ca}^{++}$ ,  $6 \times 10^{-8}$  cm;  $\text{H}^{+}$ ,  $9 \times 10^{-8}$  cm;  $\text{HPO}_4^{--}$  and  $\text{H}_2\text{PO}_4^{-}$ ,  $4 \times 10^{-8}$  cm.

## APPENDIX 2

Expressions for the calculation of the partial derivatives used in text.

The expressions given in this Appendix are based on the equations in Appendix 1.

$$\frac{d\gamma_\ell}{dI} = \gamma_\ell \frac{\Phi(I)}{2I(1+B\alpha_\ell\sqrt{I})} \quad (50)$$

in which

$$\Phi(I) = - \frac{AZ_\ell^2 \sqrt{I}}{1+B\alpha_\ell\sqrt{I}}$$

$$\left( \frac{\partial I}{\partial C_1} \right)_{c_1, H, \gamma_\ell} = 2 + \frac{G}{2f_2} \quad (51)$$

$$\left( \frac{\partial I}{\partial C_2} \right)_{c_1, H, \gamma_\ell} = \frac{G}{2f_2} \quad (52)$$

$$\left( \frac{\partial I}{\partial H} \right)_{c_1, c_2, \gamma_\ell} = \frac{1}{2\gamma_4} + \frac{(C_1 + C_2)}{2f_2 K_2} \left[ \frac{1}{\gamma_1} - \frac{G}{f_2} \left( \frac{2H}{K_1} + \frac{1}{\gamma_1} \right) \right] \quad (53)$$

APPENDIX 2 (continued 2)

$$\left(\frac{\partial I}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1 + C_2)}{2f_2 K_2 \gamma_1^2} \left[ \frac{G}{f_2} - 4 \right] \quad (54)$$

$$\left(\frac{\partial I}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{\ell \neq 4}} = - \frac{H^2}{2\gamma_4^2} \quad (55)$$

$$\left(\frac{\partial a_1}{\partial C_1}\right)_{c_2, H, \gamma_{\ell}} = \frac{(2C_1 + C_2) \gamma_3}{f_2} \quad (56)$$

$$\left(\frac{\partial a_1}{\partial C_2}\right)_{c_1, H, \gamma_{\ell}} = \frac{C_1 \gamma_3}{f_2} \quad (57)$$

$$\left(\frac{\partial a_1}{\partial H}\right)_{c_1, c_2, \gamma_{\ell}} = - \frac{(C_1^2 + C_1 C_2) \gamma_3}{f_2^2 K_2} \left( \frac{2H}{K_1} + \frac{1}{\gamma_1} \right) \quad (58)$$

$$\left(\frac{\partial a_1}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1^2 + C_1 C_2) \gamma_3 H}{f_2^2 K_2 \gamma_1^2} \quad (59)$$

$$\left(\frac{\partial a_1}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{\ell \neq 2}} = \frac{(C_1^2 + C_1 C_2) \gamma_3}{f_2^2 \gamma_2^2} \quad (60)$$



APPENDIX 2 (continued 3)

$$\left(\frac{\partial a_1}{\partial \gamma_3}\right)_{c_1, c_2, H, \gamma_{\ell} \neq 3} = \frac{(C_1^2 + C_1 C_2)}{f_2} \quad (61)$$

$$\left(\frac{\partial a_2}{\partial C_2}\right)_{c_1, H, \gamma_{\ell}} = \left(\frac{\partial a_2}{\partial C_1}\right)_{c_2, H, \gamma_{\ell}} = \frac{H}{f_1 K_1} \quad (62)$$

$$\left(\frac{\partial a_2}{\partial H}\right)_{c_1, c_2, \gamma_{\ell}} = \frac{(C_1 + C_2)}{f_1^2 K_1} \left(f_1 + \frac{K_2}{H \gamma_2} - \frac{H}{K_1}\right) \quad (63)$$

$$\left(\frac{\partial a_2}{\partial \gamma_1}\right)_{c_1, c_2, \gamma_{\ell} \neq 1} = \frac{(C_1 + C_2) H}{f_1^2 K_1 \gamma_1^2} \quad (64)$$

$$\left(\frac{\partial a_2}{\partial \gamma_2}\right)_{c_1, c_2, \gamma_{\ell} \neq 2} = \frac{(C_1 + C_2) K_2}{f_1^2 K_1 \gamma_2^2} \quad (65)$$

$$\left(\frac{\partial E}{\partial C_1}\right)_{c_2, H, \gamma_{\ell}} = 2 - \frac{Q}{f_2} \quad (66)$$

$$\left(\frac{\partial E}{\partial C_2}\right)_{c_1, H, \gamma_{\ell}} = - \frac{Q}{f_2} \quad (67)$$

# APPENDIX 2 (continued 4)

$$\left(\frac{\partial E}{\partial H}\right)_{c_1, c_2, \gamma_\ell} = \frac{1}{\gamma_4} - \frac{(C_1 + C_2)}{f_2 K_2 \gamma_1} \left(1 - \frac{Q}{f_2}\right) \quad (68)$$

$$\left(\frac{\partial E}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1 + C_2)H}{f_2 K_2 \gamma_1^2} \left(1 - \frac{Q}{f_2}\right) \quad (69)$$

$$\left(\frac{\partial E}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{\ell \neq 2}} = \frac{(C_1 + C_2)}{f_2 \gamma_2^2} \left(2 - \frac{Q}{f_2}\right) \quad (70)$$

$$\left(\frac{\partial E}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{\ell \neq 4}} = - \frac{H}{\gamma_4^2} \quad (71)$$



## REFERENCES

1. Higuchi, W. I., Gray, J. A., Hefferren, J. J., and Patel, P. R., J. Dent. Res. 44, 330 (1965).
2. Gray, J. A., and Francis, M. D., in "Mechanisms of hard tissue destruction", AAAS, Washington, D. C., 1963.
3. Holly, F. J., and Gray, J. A., (Abstract), IADR, 44th General Meeting, Miami Beach, 1966.
4. Onsager, L., Phys. Rev. 37, 405 (1931).
5. Onsager, L., Phys. Rev. 38, 2265 (1931).
6. Onsager, L., Ann. N. Y. Acad. Sci. 46, 241 (1945).
7. Dunn, R. L., and Hatfield, J. D., J. Phys. Chem. 69, 4361 (1965).
8. Edwards, O. W., Dunn, R. L., Hatfield, J. D., Huffman, E. O., and Elmore, K. L., J. Phys. Chem. 70, 217 (1966).
9. Edwards, O. W., and Huffman, E. O., J. Phys. Chem. 63, 1830 (1959).
10. Wendt, R. P., J. Phys. Chem. 69, 1227 (1965).
11. Miller, D. G., J. Phys. Chem. 63, 570 (1959).
12. Moreno, E. C., Gregory, T. M., and Brown, W. E., J. Res. NBS 70A, 545 (1966).

13. Moreno, E. C., Gregory, T. M., and Brown, W. E., NBS Report No. 1967.
14. Kirkwood, J. G., Baldwin, R. L., Dunlop, P. J., Gosting, L. G., and Kegeles, G., J. Chem. Phys. 33, 1505 (1960).
15. Hooyman, G. J., Holtan, H., Jr., Mazur, P., and de Groot, S. R., Physica 19, 1095 (1953).
16. Dunlop, P. J., and Gosting, L. G., J. Phys. Chem. 63, 86 (1959).
17. Prigogine, I., Bull. Classe Sci. Acad. roy. Belg. 34, 930 (1948).
18. de Groot, S. R., and Mazur, P., "Non-Equilibrium Thermodynamics", Interscience Publishers, Inc., New York, N. Y., 1962.
19. Gosting, L. G., in "Advances in Protein Chemistry", Vol. XI, Academic Press, Inc., New York, N. Y., 1956.
20. Prigogine, I., "Introduction to Thermodynamics of Irreversible Processes," Interscience Publishers, Inc., New York, N. Y., 1961.
21. Wendt, R. P., J. Phys. Chem., 66, 1279 (1962).
22. Bates, R. G., J. Res. NBS 47, 127 (1951).



23. Bates, R. G., and Acree, S. F., J. Res. NBS 34, 373 (1945).
24. Selvaratnam, M., and Spiro, M., Trans. Faraday Soc. 61, 360 (1965).
25. Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions", Academic Press, Inc., New York, N. Y., 1959 p. 463.
26. Tatarinov, B. P., and Fursenko, V. F., Russian J. Phys. Chem. 34, 62 (1960).
27. Manov, G. G., Bates, R. G., Hamer, W. J., and Acree, S. F., J. Am. Chem. Soc. 65, 1765 (1943).
28. Kielland, J. J., J. Am. Chem. Soc. 59, 1675 (1937).





